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Authors

Coll, I
Rousseau, C
Barletta, B
et al.

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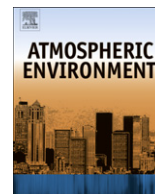
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Evaluation of an urban NMHC emission inventory by measurements and impact on CTM results

Isabelle Coll^{a,*}, Cécile Rousseau^{a,b}, Barbara Barletta^c, Simone Meinardi^c, Donald R. Blake^c

^a LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques), UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, CMC, 61 avenue du Général de Gaulle, 94 010 Créteil Cedex, France

^b LCP (Laboratoire Chimie Provence), UMR CNRS 6264, Pôle Environnement, Université de Provence, Campus St Charles, 3 place Victor Hugo, 13331 MARSEILLE Cedex 3, France

^c Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

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ABSTRACT

This paper presents an evaluation of the consistency of an urban state-of-the-art hydrocarbon (HC) emission inventory. The evaluation was conducted through the comparison of this inventory with hourly HC measurements during two summer months in the centre of Marseille, on the Mediterranean French coast. Factors of under or overestimation could be calculated for each compound on the basis of a systematic HC to HC ratio analysis. These results, associated with a deep analysis of the speciation profiles, show that most of the common and highly concentrated hydrocarbons (such as butanes) are too much predominant in the emission speciation, while the heavy and less common species (branched alkanes, substituted aromatics) are under-represented in the inventory. The urban diffuse sources appear here as one critical point of the inventories. The disagreements were shown to have a strong incidence on the representation of the air mass reactivity. In a last step, the identified uncertainties in emissions were implemented in an air-quality model for sensitivity studies. It was shown that the observed biases in the inventory could affect the regional ozone production, with a probable impact on ozone peaks of 2–10 ppbv over the area.

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1. Introduction

Volatile organic compounds (VOCs) hold a determining place in air-quality-related problems at various scales in the troposphere (Colville et al., 2001; Friedrich and Obermeier, 1999; Sillman, 1999) due to their intense emission at ground level and their fast reactivity with OH in the presence of nitrogen oxides (NO_x) to produce ozone and oxidized species. The numerous field research works conducted during the last twenty years provided an important knowledge about their presence in the lower atmosphere and their role in the formation of ozone (Solomon et al., 2000). However, numerous questions remain, principally related to the characterization of VOC urban emissions and to their impact on rural and remote environments. In urban areas indeed, it is necessary to complete our knowledge on the mixing of VOC sources to better evaluate the exposure of the population to gaseous pollutants (ORSIF, 2006), and to produce a consistent description of regional anthropogenic plumes and their related ozone formation potential (here called OFP). Such regional studies are commonly

apprehended through Chemistry-Transport Models (CTMs), which are used in supports to national environmental policies to estimate the relevance and the efficiency of the emission abatement strategies on the regional production of ozone.

In the CTMs, the good representation (quantities, temporal and spatial distribution) of primary pollutant emissions governs the relevance of the simulated concentration fields. The emission inventories used in CTMs have strongly evolved during the past ten years in view of the necessity to increase their accuracy. In particular, the elaboration of reliable methodologies for VOC source inventory such as CORINAIR (or COPERT for mobile sources, <http://www.tremove.org/meetings/20060330%20Zisis%20Samaras.pdf>) led to the establishment of spatialized emission inventories with an increased refinement and complexity. However, day-to-day VOC emissions over a selected region remain in most cases inferred from mean annual activity data, calculated from standard emission factors by sector of activity, and disaggregated at an hourly time step according to pre-defined temporal profiles. According to a recent air-quality assessment in North-America (NARSTO, 2005), one delicate stage of the generation of emission inventories is the representation of the wide variety of VOC species emitted by each source, because of the weakness of some existing speciation

* Corresponding author. Tel.: +33145171546.

E-mail address: isabelle.coll@lisa.u-pec.fr (I. Coll).

profiles, which may be erroneous, non-existent or unsuitable for particular sources or locations. A report of the US National Research Council (2004) highlights other domains in which a significant progress is necessary: in particular, this report indicates that industrial point sources are correctly taken into account in the inventories, but that it is not the case of the majority of the diffuse sources (industrial urban activity, namely). Both studies insist on the need for the identification and the quantification of the uncertainties in emission inventories from field campaigns, which remain one of their largest weaknesses.

The evaluation of emission inventories from field data is a complex task. Many factors influence the concentrations of pollutants measured in the atmosphere, such as emissions, transport, transformation, deposition, and geographical specificities of the measurement site, which are highly difficult to account for and to isolate. These technical difficulties justify the lack of data on this subject. In urban areas, many studies focused on VOC measurements in city centres, on the evaluation of their individual source profiles or emission ratios (e.g. Derwent, 2000; Dollard et al., 2007; Kalabokas et al., 2001; Touaty and Bonsang, 2000), and on source apportionment studies with Chemical Mass Balance models that allowed the identification and contribution, at a given point, of the main VOC sources (e.g. Guo et al., 2007; Watson et al., 2001). These studies provided a hierarchical view of the VOC present in urban areas, and helped identifying the main sources affecting local air quality. All the studies pointed out the predominance of road traffic in affecting urban air composition. They also helped reducing the uncertainties in emission profiles and intensity. Despite those advances, large differences between measurements and emission model outputs are still noted. Two European studies, discussed in Theloke and Friedrich (2007), reported that modelled urban hydrocarbon concentrations (normalized to CO so as to get rid of meteorology effects) differed from observations by a factor of 2 (ESQUIF experiment in Paris) to 10 (EVA experiment), the highest discrepancies being observed for solvent related species such as n-nonane and n-decane, propylbenzene and 1,3,5-trimethylbenzene.

These results support the need for supplementary works on the accuracy of urban emission inventories in urban areas. The present study focuses on the global representativeness of an urban Non-Methane HydroCarbon (NMHC) mixture, as provided by a state-of-the-art urban emission inventory compiled by LPCA/CGS (University L. Pasteur, Strasbourg, France) in collaboration with the regional air-quality network Atmo PACA at Marseille under the supervision of the national environmental agency ADEME (François et al., 2005). It is described in more details below. From several sets of NMHC measurements, we propose a critical evaluation of emission speciation profiles. We aim to better address the way emission inventories represent the real urban NMHC mixture described by field experiments and how much the identified gaps can affect regional ozone forecasts.

For this purpose, we used measurements made within the framework of the ESCOMPTE project in a polluted region of Southern Europe: the city of Marseille and the neighbouring huge industrial Berre complex, located on the French Mediterranean coast (see Fig. 1). The present study focuses on the evaluation of the urban part of the emission inventory built up within the ESCOMPTE framework. After describing the region and discussing our methodology, we first evaluate the modelled NMHC emission speciation for the whole urban area and for selected activity sectors. In a second part, we run the CHIMERE CTM on a highly polluted period of the ESCOMPTE campaign to discuss the impact of the uncertainties in the inventory. This model is dedicated to the interpretation of regional-scale measurement campaigns, but it is also used by national and regional institutes for real-time air-quality forecasts (Honoré et al., 2008; Vautard et al., 2003).

2. Site of the study and methodology

2.1. The ESCOMPTE project and the associated databases

The ESCOMPTE program (conducted in summer 2001) was designed to closely evaluate and improve CTMs at the regional scale. It was based on a vast field campaign, offering a 3D description of dynamical and chemical parameters of the troposphere during episodes of photochemical pollution. The ESCOMPTE campaign (Cros et al., 2004) constitutes a reference data set, which, beyond its use in regional CTMs, allowed the investigation of multiple aspects of photochemical pollution such as the meteorological and chemical specificities of the land–sea breeze, or the impact of local emission scenarios on air quality (Drobninski et al., 2007). The region selected for this project is located along the French Mediterranean coast (Fig. 1). It contains the conglomeration of Aix-Marseille (1 million inhabitants) and the industrial complex of Fos-Berre located 50 km at the North-west of Marseille, around the Berre pond. This region experiences the largest number of exceedances of the 1-h information limit for ozone (90 ppbv) in summer among the different urban centres in France.

During the field campaign, physical and chemical measurements were conducted at the surface and in altitude, over the continent and offshore. In particular, dedicated hydrocarbon (HC) measurements were performed at several sites characterized by intense primary emissions, over short time periods (24–72 h). They allowed the characterization of NMHC emission profiles for several types of industrial and urban emitters in the region. The measurements were carried out by the University of California Irvine (UCI). Ambient air was sampled in electropolished stainless steel canisters with a filling time of approximately 2 min. Details about the analysis method can be found in Colman et al. (2001). Briefly, 790 cm³ of air were cryogenically preconcentrated at –196 °C in liquid nitrogen, and subsequently vaporized and split into five different column/detector combinations, the detectors being two Flame Ionization Detectors (FIDs), two Electron Capture Detectors (ECDs) and a Mass Spectrometer Detector (MSD). A total of 122 samples were collected and 77 compounds were identified, including 47 NMHCs. In parallel, continuous measurements of 53 NMHC atmospheric levels were conducted in the centre of Marseille in June and July 2001 with an hourly time step, by the Atmo PACA air-quality network (964 samples) in charge of air-quality monitoring over the Provence – Alpes – Côte d'Azur (PACA) region. These measurements were made in the middle of a dense urban infrastructure but not directly along the largest road-traffic axes, which allowed a representative sampling of the standard mixture of urban sources: traffic-related emissions, residential emissions, but also small emitters such as those existing nearby the site (garages, gas stations, printing offices, and laundries). Then, the site could sample any diffuse source that affects the city, without being too close of any specific emitter. The measurement site is called “Marseille-Prado” due to its location close to the Prado Avenue. The measurement method includes a pre-concentration step on a solid adsorbent during 32 min and its analysis by gas chromatography coupled with a flame ionization detector. In this case, the long sampling time allows the minimizing of the impact of very punctual interferences (car passing) on the sample composition. At this site, several samples were also collected by UCI over a few week period. On the basis of 19 coincident UCI and Atmo PACA sampling events at this specific location both datasets were tested, validated (Rousseau, 2008) and used in this work.

The ESCOMPTE emission inventory was built following a bottom-up approach and delivered hourly at a resolution of 1 km. For the anthropogenic, biogenic, and natural sources, the emitters were listed according to the Selected Nomenclature for Air Pollution (SNAP) methodology in its third level of detail (<http://www.eea.europa.eu/publications/EMEP/EMEP-CORINAIR3/BCOR90.pdf>). Point source emission

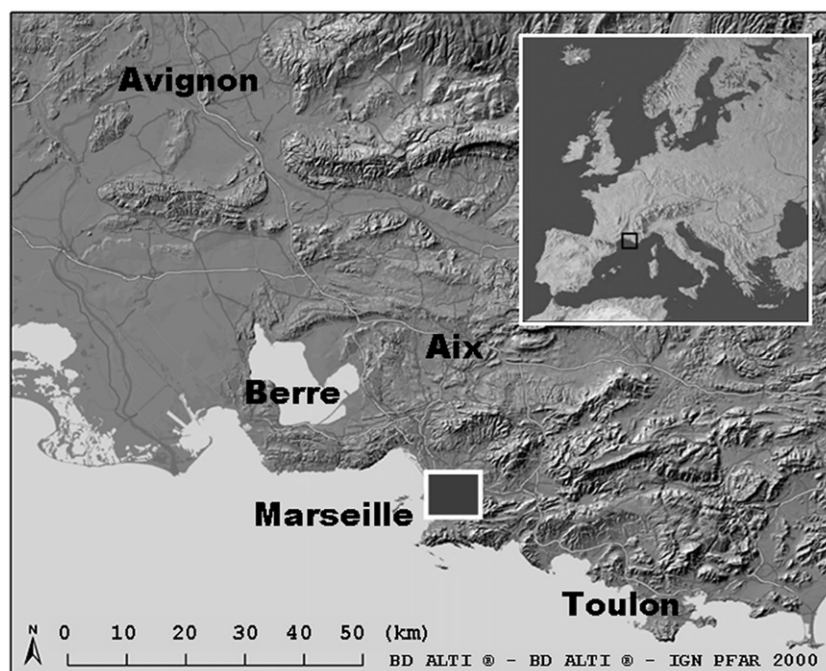


Fig. 1. Map of the area of interest. The $5 \times 5 \text{ km}^2$ square located in Marseille delimits the restricted area used for the inventory–observations comparison.

data come from the regulatory control of industrial and public installations and include several data sources: the official listing of companies and industries (Système d'Identification du Répertoire des ENTREPRISES), the census of the population and activity sectors for 1999 (Institut National des Statistiques et des Etudes Economiques), and land use data (Centre Régional de l'Information Géographique). For road traffic, the COPERT III classification (Ntziachristos et al., 2000) was chosen, and was completed by the Nomenclature for Air Pollution of FUEL oils – NAPFUE – (EEA, 2002). Mobile source emissions were estimated from the evaluation of traffic intensity and from the composition of the local car fleet made by the INRETS (Institut National de Recherche sur les Transports et leur Sécurité), in combination with the census of the regional road network from IGN (Institut Géographique National) databases. For combustion emissions, regional consumption data were obtained for each industrial activity. For production emissions (data compiled by the TNO – Netherlands Research Organization), regional production statistics were used when available. When they were not available, calculations were made on the basis of national production data crossed with the number of people working in each activity. For fuel extraction and distribution, and for solvent use activities, the data were extracted from the SIRENE database. The emissions of companies that correspond to the targeted activities (application of paint, degreasing, dry cleaning, electronics, manufacturing and implementation of chemical products, other uses of solvents and associated activities) were considered. For spatial allocation, all data were crossed with the CRIGE 121 database (indicating industrial and commercial zones) and with the population database, for the activities that are known to depend upon population. More details about the constitution of this inventory can be found in François et al. (2005).

2.2. Methodology and strategy

2.2.1. Methodology for data analysis

To evaluate the emission inventory against observations, we extracted the emission data over an area of $5 \times 5 \text{ km}^2$ with high urban density corresponding to the urban centre of Marseille and

including the measurement site (see the area in Fig. 1). This area of the inventory well compares with the measurement site: its dimension allows to take into account the close diffuse sources most likely affecting the measurement point, but also to ignore the point sources located outside the city centre, that appear to be too distant to be intensely collected on the site (see the detailed analysis of local influences in Rousseau, 2008). We summed the emission data over this small area to obtain hourly and daily emitted quantities of the NMHCs, for all emitters as well as for selected SNAP activities. These data were then processed into mass percentages of the total emissions, allowing the generation of mass speciation profiles.

Our first goal was to evaluate the global representativity of the inventory over the city centre. We thus compared the average observed (measurements) and calculated (inventory) NMHC mass profiles over the urban zone, on the basis of 41 NMHC (Table 1) that were common to the inventory and to the observations. Then, we tried to identify which individual NMHC percentage was underestimated or overestimated in the inventory. Indeed, the calculation of a hydrocarbon to hydrocarbon ratio does not constitute a self-sufficient information because it does not make possible to determine which hydrocarbon is badly estimated. We thus proceeded to the systematic calculation of the ratios of every HC_a to each of the other HC_i in the emission inventory (noted $(\text{HC}_a/\text{HC}_i)_{\text{EI}}$) and in the observations (noted $(\text{HC}_a/\text{HC}_i)_{\text{OBS}}$). We represented these 2 sets of values in a scatter plot, and analyzed their distribution around a line of slope $s = 1$, symbolizing a total agreement between both databases. This graph allowed us to define several compounds for which data lay around the line of slope 1, and on the contrary to identify the hydrocarbons characterized by a mass percentage greatly different from that in observations, with many of their points laying far from the ideal slope. A degree of over/under estimation of the part of such hydrocarbons HC_a in the mass speciation was then derived by calculating the average value of the $[(\text{HC}_a/\text{HC}_i)_{\text{EI}} - (\text{HC}_a/\text{HC}_i)_{\text{OBS}}]$ ratio, HC_i being the compounds which appear to be well estimated in this test.

Table 1

List of the 41 Non-Methane-Hydrocarbons common to the observations and to the inventory.

Alkanes	Alkenes and alkynes	Aromatics
ethane	ethylene	benzene
propane	propene	toluene
iso-butane	1,3-butadiene	2-ethyltoluene
n-butane	1-butene	3-ethyltoluene
iso-pentane	2-butene	4-ethyltoluene
n-pentane	iso-butene	ethylbenzene
2,2-dimethyl butane	1-pentene	m + p-xylene
2,3-dimethyl butane	2-pentene	o-xylene
2-methylpentane	1-hexene	styrene
3-methylpentane		1,2,3-trimethyl benzene
n-hexane	acetylene	1,2,4-trimethylbenzene
2-methylhexane		1,3,5-trimethyl benzene
3-methylhexane		iso-propyl benzene
n-heptane		n-propylbenzene
iso-octane		
n-octane		
n-nonane		

This approach was completed by a graphic analysis of the speciation of urban sources in the inventory, and its components presented by sector of activity, compared with the profiles derived from urban measurements and from measurements close to specific emitters. It allowed us to clarify the origin of the differences between the inventory and the observations that were highlighted in the first part of our analyses.

We finally estimated the incidence of these uncertainties on the representation of the “ozone formation potential” of a young urban air mass. The method we adopted for the calculation of this OFP is a reactivity-based method using the concept of “propylene-equivalent concentration” presented in Chameides et al. (1992). For a given hydrocarbon i , it is a calculation of the concentration (in ppbC) of propylene required to reach the same oxidation rate as the original hydrocarbon i under its own concentration. It is obtained by the following equation

$$[\text{propy} - \text{equiv}]_i = n_{Ci} \cdot [\text{HC}]_i \cdot \frac{k_i^{\text{OH}}}{k_{\text{C}_3\text{H}_6}^{\text{OH}}}$$

where n_{Ci} is the number of carbon atoms of HC_i , $[\text{HC}]_i$ is its molar ratio and k_i^{OH} is the rate constant of the reaction of HC_i with the OH radical. This equation allows to easily compare the ability of each hydrocarbon, in the urban environment, to react with atmospheric radicals and to produce ozone.

2.2.2. Model study

To address the question on how important are the impacts of the inventory uncertainties on CTM outputs, we tried in a last step to evaluate the degree of sensitivity of CTMs to variations in input emission profiles, when used for regional modelling. CTMs indeed have shown to be able to correctly reproduce the dependence between precursors and ozone beyond a resolution of 5 km (Cohan et al., 2006) and to find an acceptable agreement with measures when they are made reasonably apart from the points of dense emissions.

This study was conducted with the eulerian model CHIMERE, which is dedicated to air-quality forecasting and photo-oxidant pollution analysis from the regional to the continental scale (<http://www.lmd.polytechnique.fr/chimere/>). The model was run in a configuration especially designed within the framework of the ESCOMPTE project to optimize the model accuracy with respect to the available data (see Lasry, 2006; Lasry et al., 2007). In particular, a condensed version of the chemical scheme SAPRC99, which

represents the state-of-the-art as of mid 1999, was implemented into CHIMERE. This mechanism uses the lumped molecule approach, and describes the chemistry of 82 species including 2 primary organics (ethylene and isoprene) and 10 lumped species representing hydrocarbons (Carter, 2000). This scheme was evaluated against a large number of chamber experiments and considered as reasonably successful in predicting ozone formation from complex urban mixtures (Carter, 1990). High-resolution dynamic fields were calculated with the MM5 model (<http://www.mmm.ucar.edu/mm5/>). Boundary conditions were provided by a continental-scale simulation of CHIMERE. The simulation domain has been set to a width of 140 km, with a horizontal resolution of 4 km and 15 levels on the vertical, up to 3000 m. The emissions were extracted from the ESCOMPTE spatialized inventory and were aggregated to fit the model resolution and the lumped SAPRC99 chemical species.

The CHIMERE outputs, for all the ESCOMPTE observation periods, have been closely evaluated within the framework of a CTM intercomparison exercise associated to the project, and through classic statistical indexes of measurement–model comparison. These analyses revealed a satisfactory behaviour of the model on the area with very few missed exceedances of the ozone regulatory thresholds and a good representation of the ozone plume location and intensity (see Coll et al., 2009 for more details). The CHIMERE model was run in this validated configuration for a selected 4-day period running from 23 to 26 June 2001, which corresponds to the main pollution episode of the ESCOMPTE campaign, and representing the most common meteorological pollution situation of the region. Measurement versus model time series for primary compounds allowed us to highlight the main strengths and weaknesses of the inventory. We then ran the model again several times, with modified NMHC emission speciations. The random perturbation of the NMHC profile was set within the range of the uncertainties highlighted by the initial HC ratio tests. The sensitivity of the modelled ozone field concentrations to the different NMHC emission profiles resulting from the perturbation of NMHCs is discussed in the last part of this work.

3. Results and discussion

3.1. Representation of the urban source mixing

The sector distributions of the NMHCs (in mass percentage) are represented in Fig. 2 for the observations (on the left) and for the emission inventory (on the right). The figure is restricted to the Marseille centre area defined above, for the common set of 41 NMHCs. Although a global agreement can be found in these distributions, this figure reveals a pronounced tendency of the emission inventory to overestimate alkenes (20% versus 10%), while the parts of the heavy alkanes and of the benzene–toluene–ethylbenzene–xylene (BTEX) family are – on the contrary – lower in the emission speciation than in the measurements.

A more precise picture could be drawn when looking at the individual compounds. The first results revealed a very high overestimation of ethylene (factor larger than 10) in the emissions. A close examination of the inventory methodology allowed us to affirm that the pronounced overestimation of ethylene, but also to a much lesser extent that of acetylene, propene, benzene and 1,3-butadiene, can be attributed to an excessive representation of wood combustion inside residential (SNAP 2) and commercial (SNAP 3) combustion activities in the inventory. These activities respectively correspond to residential and manufacturing boiler use, not only for house heating but also for water heating, cooking etc. Thus, they normally appear in a summer emission inventory. The problem comes from the use of a regional activity database that does not

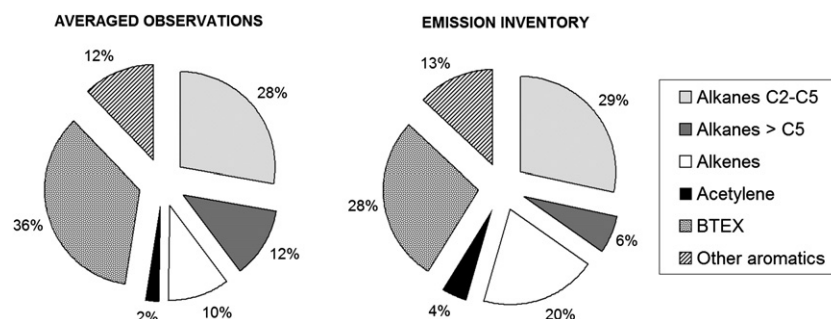


Fig. 2. Distribution (in mass percentage) of the hydrocarbon families in the observations (left graph, averaged value over June–July 2001) and in the emission inventory (right panel, mean diurnal value).

distinguish urban from rural residential combustion specificities and does not take into account the park of heaters. Thus wood burning, which is very common in the North-eastern rural areas of our domain and is absent in Marseille, was wrongly introduced in the Marseille emission inventory, leading to large emissions of specific compounds such as ethylene. Furthermore, as no local data could be collected for this specific area source, its distribution over the region was made by default according to population density. As often in this case, this led to the overestimation of global urban combustion emissions. We can see here that the correct representation of urban combustion is a relevant issue for HC emission inventories, even in summer. This issue could be even more critical for particulate matter, as wood combustion is considered as a strong emitter of particles in the atmosphere (Dilara, 2004). In order to avoid disturbance by this problem, ethylene was removed from our calculations. The emission-measurement comparison of all other individual hydrocarbons, sorted by family and number of carbon atoms, is presented in Fig. 3. When looking at the representation of major and minor species, the speciation of the urban HC mixture appears well understood by the inventory. However, among the main elements of this speciation, high discrepancies are observed between emissions and observations (i.e. +51% for benzene, –43% for iso-pentane, a factor of 2.5 for n-butane). In particular, we can observe strong discrepancies for alkanes, with the inventory favouring the emission of light species against heavy ones. The first seven alkanes of this distribution indeed represent 86.1% of the total alkanes in the inventory against 73.3% in the observations. This

overestimating trend is especially observed on butanes, a remarkable exception being iso-pentane. Except for n-nonane, the last 9 alkanes of this distribution then present an underestimation of their percentage compared to measurements, by a factor of 2–3 for many of them and up to a factor of 9 and 10 for 2,2-dimethylpentane and iso-octane, respectively. No specific trend is observed for alkenes. Among the aromatics, we can see that the mass percentage of benzene is overestimated by the inventory while m/p-xylene, ethylbenzene and 2-ethyltoluene appear underestimated. However, the rest of the aromatic compounds seem to present a “distribution” that is very close to the observations. In spite of the observation of clear tendencies, this figure does not allow us to define which NMHC are actually overestimated in the inventory with regards to the others, because a bad representation of a single compound (e.g. for n-butane) can alter the whole speciation profile. We thus used the “HC_a to all HC_i” ratios described in the previous section. We calculated these ratios for each one of the 40 remaining NMHCs of our study.

Fig. 4 shows (in black squares) the ratios calculated for 6 hydrocarbons to each of the other HC_i. The whole set of ratios (circles) is reported in every graph and allows to infer the global trends of the emission–observation comparison. First of all, we can observe that the obtained ratios lie rather well along the line of slope 1, which reflects a good overall consistency. However, the smallest values (on the left) appear underestimated by the inventory as the calculated ratios mainly remain under the line, whereas the strongest values (on the right) appear overestimated, above the

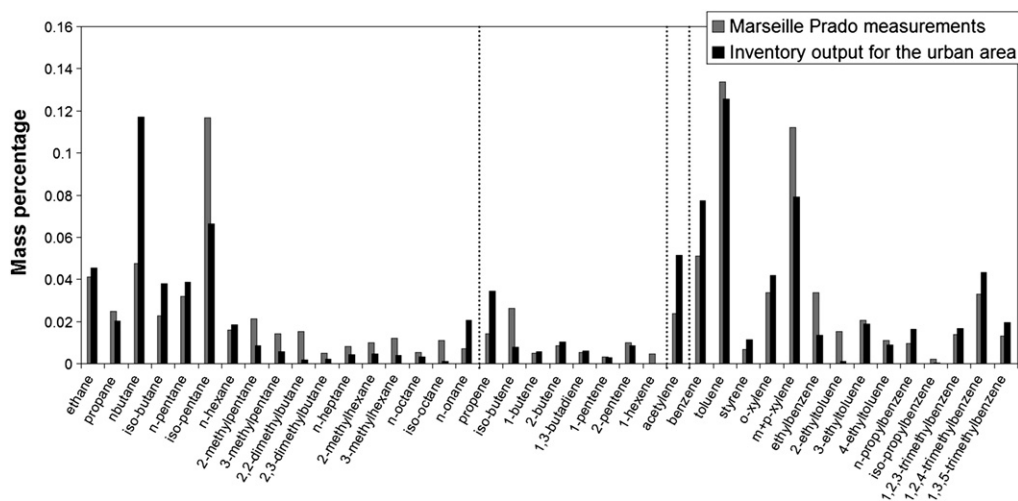


Fig. 3. Inventory output (diurnal mean speciation) for the urban area, in black, compared to the mean diurnal speciation extracted from the Atmo PACA observations, in grey, for 40 common NMHCs.

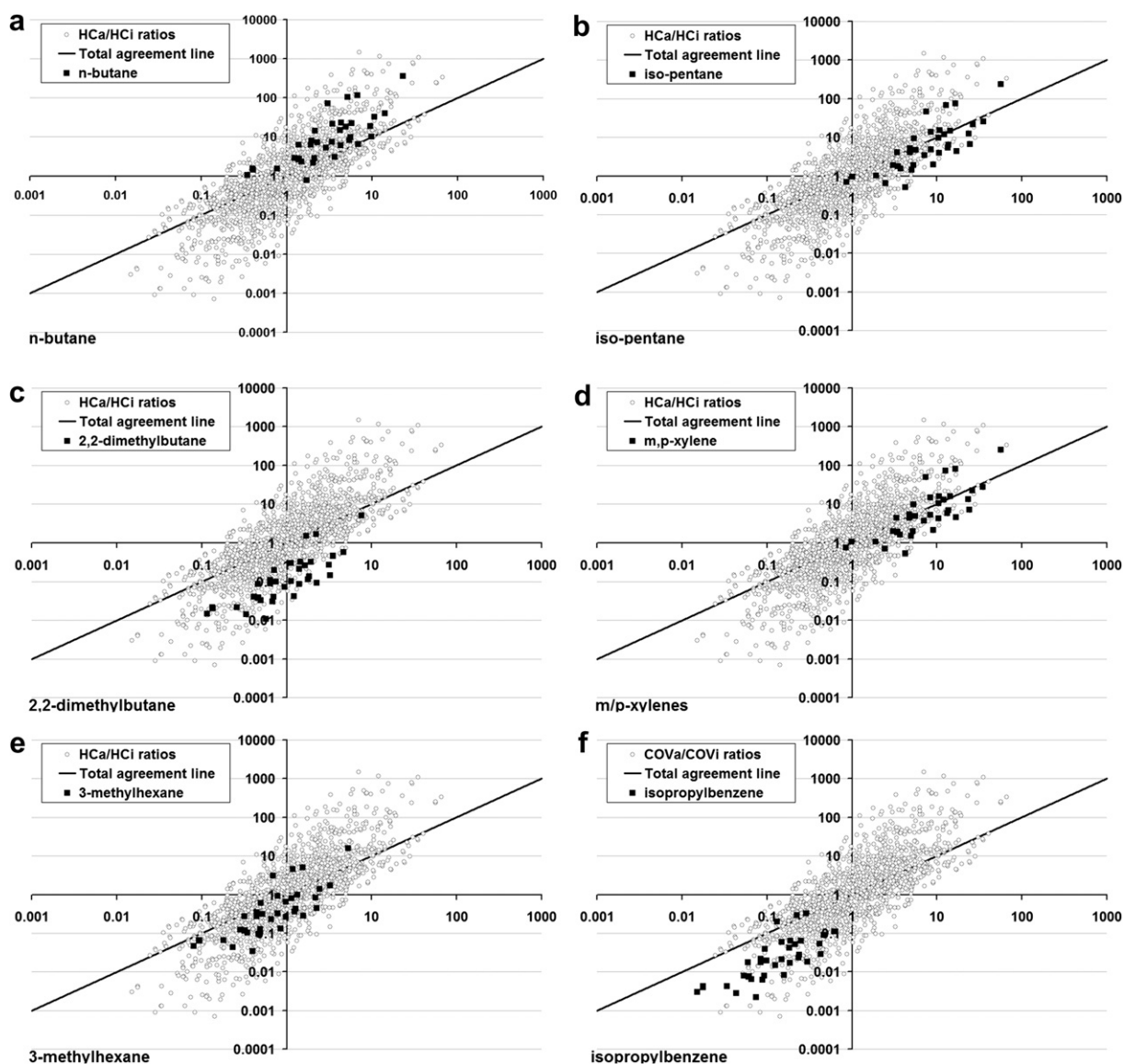


Fig. 4. a–f graphs : HCa/HCI ratios for all HCa (white dots) and for a given HCa (in black) in the inventory (y axis) versus the observations (x axis). The line corresponds to a perfect agreement between the two datasets.

line. This feature denotes an over-representation of the most abundant hydrocarbons (generating large ratios) at the expense of the minor ones. The inventory thus presents a speciation profile much less detailed than that obtained from the measurements, by exaggerating the parts of the well-known simple species. We have chosen to present here 6 compounds, representative of the sources present in this region (see Rousseau, 2008, and references therein) and of the main anthropogenic emitters (Dore et al., 2006):

- n-butane (both associated with combustion processes and refineries and Liquefied petroleum gas (LPG))
- iso-pentane (strongly associated with road-traffic and fuel distribution)
- 2,2-dimethylbutane (essentially associated with road traffic)
- m- and p-xylene (5th main compound measured in the tunnels in Marseille, but also emitted as a solvent)
- 3-methylhexane (mainly known as a gas evaporation product, but also emitted as a solvent over the area)
- iso-propylbenzene (mainly emitted as a solvent)

The compounds that are closest to the line are benzene, ethane and propane. The results of this approach put in evidence a clear overestimation of the participation of linear or low-ramified alkanes such as iso-butane, n-butane (Fig. 4a), n-pentane, and nonane, which are already major components of the speciation, while the branched alkanes are too weakly represented in the inventory compared to measurements (see 2,2-dimethylbutane in Fig. 4c as an illustration). They bring to light a structural bias in the inventory. On the reverse, while iso-pentane (Fig. 4b) and iso-octane (not shown) are major and low-ramified components of the emissions, their part don't appear as overestimated, and are even underestimated. Their cases require further investigation, to elucidate if the disagreement between observations and the inventory indicates errors in the road-traffic combustion speciation profile, or if they highlight the lack of representation of another source. For iso-pentane, this last hypothesis appears likely, as it is a component of gasoline evaporations, and recent works show that this phenomenon is weakly represented in emission inventories, while it is supposed to constitute an important fraction of

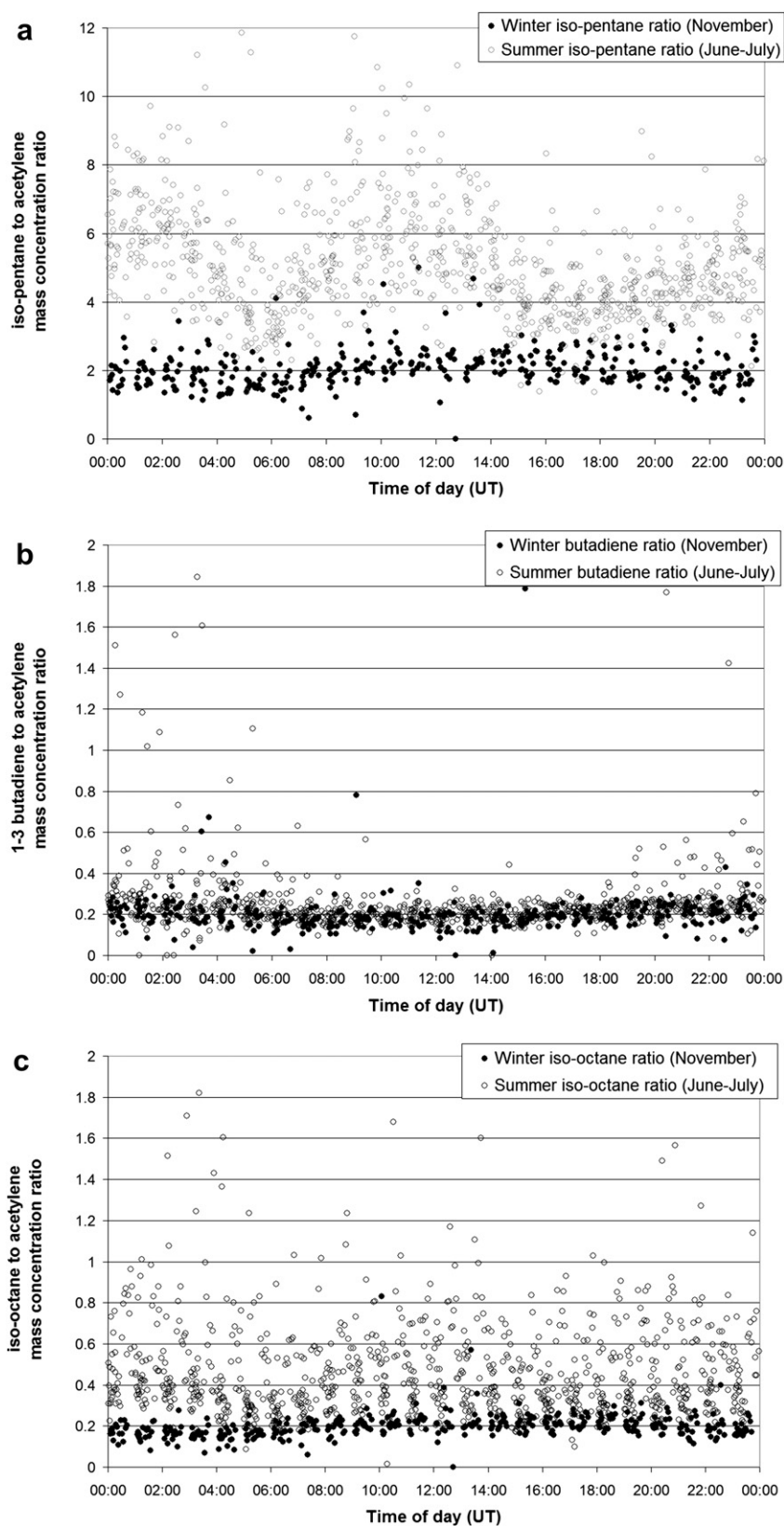


Fig. 5. Winter (black dots) and summer (white dots) iso-pentane to acetylene mass concentration ratio (a) as a function of time, measured at Marseille Prado in 2001. Comparison with 1–3-butadiene (b) and iso-octane (c) ratios to acetylene.

emissions in an urban environment (Borbon et al., 2002; Möllmann-Coers et al., 2002). In order to observe any supplementary sources, we plotted the iso-pentane, 1–3-butadiene and iso-octane to acetylene ratios in Marseille for summer and winter (dataset obtained by Atmo PACA at the same location and with the measurement method as for summer, conducted in October and November 2001), as a function of the time of the day. A similar approach was used by Lee et al. (2006) to observe the seasonal evolution of anthropogenic NMHC emissions in rural New England. Fig. 5a presents the case of iso-pentane: as acetylene is emitted by traffic combustion only, and iso-pentane is a major component of traffic combustion, their ratio at the times of the traffic peaks mainly reflects this emitter, while any positive deviation from this value should highlight the existence of a distinct iso-pentane source. We indeed observe strong deviations from the combustion source ratio, exclusively in summer, and both during sunny hours and nighttime. This is not the case for 1–3-butadiene (see panel b) which is known to be almost exclusively emitted by combustion. During such periods, the ratio of iso-pentane to acetylene is multiplied by 2–3 as a mean. Such specificities support the hypothesis of an intense temperature-dependent evaporation phenomenon, most probably originating in urban traffic, and that still remains to be quantitatively reproduced in the inventory to fit observations. Midday increases in the ratio may derive both from hot soak (when cars just stopped and the engine is hot) and diurnal losses (when the car is parked for a long time). Nighttime increases may most probably reflect only diurnal losses, which are still supposed to be twice as high in summer as in winter and which amplitude is probably emphasized by their occurrence in a reduced vertical mixing height. The moderate underestimation of other species, such as aromatics (xylenes), could be at least partly linked to the underestimation of this phenomenon in the inventory. The iso-octane to acetylene ratio in Fig. 5c shows a pronounced seasonal behaviour with no change in summer during the morning traffic rush (iso-octane is very few emitted during combustion): as for iso-pentane, it reveals the existence of a temperature-dependent source which amplitude varies from day-to-day. Such behaviour can be attributed to the temperature-dependent evaporation of iso-octane from the surrounding urban industrial activities linked to solvent use (Rousseau, 2008). Those sources then appear as strongly underestimated in the emission inventory.

Finally, the aromatic compounds show a small but common tendency to be underestimated in the inventory, with the exception of benzene. This common behaviour supports their correct relative abundance noticed in Fig. 3. However, it is interesting to notice that complex aromatic compounds relying on solvent use such as

2-ethyltoluene (Fig. 4f) and iso-propylbenzene are clearly under-represented in the emissions. Regarding alkenes, no clear tendency is observed, except for propene – which emissions are too large here due to a bad evaluation of residential wood combustion. However, the less abundant alkene in our selection (i.e. 1-hexene) is again underestimated. Table 2 summarizes the most striking values of the disagreement factors, obtained from the method described in Section 2.2.1. It shows a large range of values for the underestimation factors (reaching up to 36 for 1-hexene) which, as mentioned above, often concern the minor components of the urban mixture: compounds emitted from diffuse urban sources implying solvent use (printing offices, paintings, garages...), but also uncommon compounds that are not frequently measured in situ. The overestimation factors, mainly relative to the predominant hydrocarbons, are less scattered.

In order to explore the emission inventory consistency into more details, we analyzed the hydrocarbon speciation profiles of particular emitters. For this task, we used data extracted from the emission inventory and data obtained through the designed HC sampling experiments conducted on the region during the 2001 ESCOMPTE campaign.

3.2. Evaluation of specific speciation profiles

Fig. 6a represents the HC mass speciation profile of the SNAP 7 subdivision of the inventory (related to road-traffic) compared with the one obtained from a canister sampling experiment (7 samples, collected on July 03 at 08:58, July 5 at 14:33 and July 11 at 11:35, 11:51, 12:02, 12:20 and 12:32) in a tunnel of Marseille. Rousseau (2008) showed that this profile was consistent with many similar road-traffic sampling experiments conducted in Europe so conclusions can be extrapolated to many urban areas. In Fig. 6b, the mass speciation of the subsector SNAP 0706 of the inventory, representing road-traffic fuel evaporations, is reported against two single measurements. The first one was conducted in a gas station in Marseille, the second one in the vicinity of a gas storage tank in an industrial area. The hydrocarbons that are common to these specific measurements and to the inventory are not exactly the same as with the continuous monitoring data, but they are ranked the same as previously. Here, ethylene data could be kept as the ethylene problem is only related to the SNAP 2 of the inventory. The representativity of these two samples is supported by their similarities (especially for volatile branched alkanes) and by their low content in combustion species (acetylene, m-/p-xylene), especially at the gas station. The case of iso-butene is not questioning: it is a common component of road

Table 2

Disagreement factors for a selection of 17 hydrocarbons which part in the speciation strongly differs between the observations and the emission inventory. The well estimated compounds used to calculate the disagreement factor are ethane, benzene and propane.

Overestimated HCs (average concentration over the summer, in $\mu\text{g m}^{-3}$, with their standard deviation)	Disagreement factor (as described in Section 2.2.1)	Underestimated HCs (average concentration over the summer, in $\mu\text{g m}^{-3}$, with their standard deviation)	Disagreement factor (as described in Section 2.2.1)
n-butane (4.26 ± 3.35)	2.6	iso-pentane (10.42 ± 7.70)	0.67
iso-butane (2.02 ± 1.84)	1.9	2-methylpentane (1.90 ± 1.48)	0.40
n-pentane (2.86 ± 2.04)	1.7	2,2-dimethylbutane (1.38 ± 1.16)	0.11
n-nonane (0.64 ± 0.72)	2.7	3-methylpentane (1.25 ± 0.78)	0.42
Ethylene (2.69 ± 2.87)	5.8	3-methylhexane (1.08 ± 1.19)	0.50
Propene (1.25 ± 0.95)	32	iso-octane (0.99 ± 1.52)	0.13
1,3-butadiene (0.48 ± 0.34)	2.5	m-p-xylenes (10.02 ± 8.01)	0.72
Acetylene (2.14 ± 1.70)	2.4	ethylbenzene ($3.01 \pm$)	0.56
		2-ethyltoluene (1.36 ± 7.64)	0.17
		iso-propylbenzene (0.19 ± 0.16)	0.17
		1-hexene (0.40 ± 0.59)	0.03

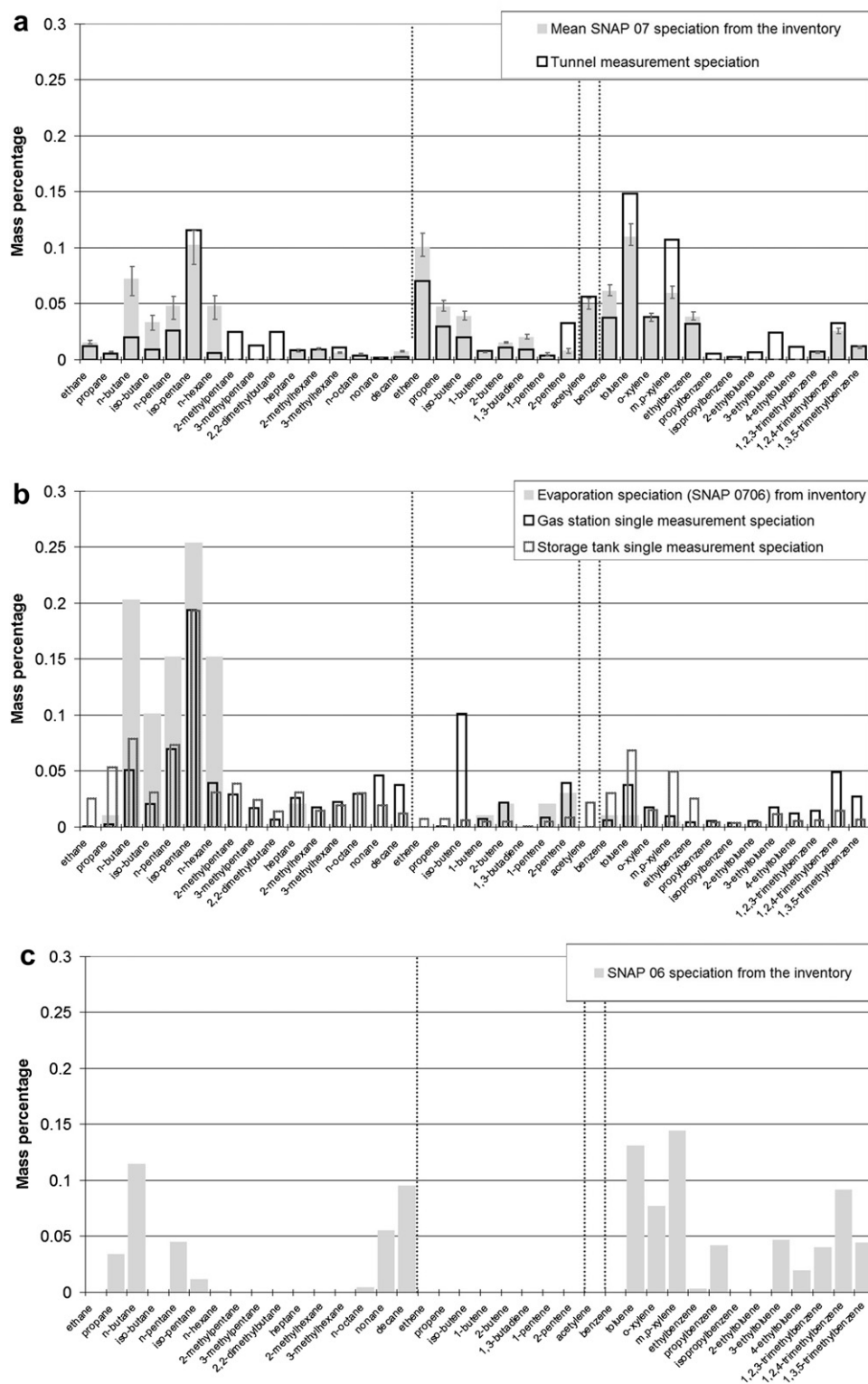


Fig. 6. Hydrocarbon mass speciation from the inventory for the 5×5 km urban area, for different sectors of activity. Comparison to measurements for figures (a) and (b).

transport and fuel-related activities (Dore et al., 2006), but its absence in the industrial area is due to the fact that this site produces a petrol cut called “C4” where iso-butene has been removed to produce a gasoline additive called MTBE (methyl tert-butyl ether). The single measurements then appear well-representative of their environment.

From a close analysis of these 2 figures, we can draw two conclusions about the representation of gas evaporation in the inventory. First, although road traffic appears as a well-known emitter (good global agreement with the tunnel measurements, concerning the nature of the main emitted species) we can notice a lack of representation of branched alkanes and branched

aromatics. Secondly, the evaporation profile of the inventory (0706) does not account at all for the variety of compounds observed in the measurements. As an illustration, the non-represented compounds make up to 43.4% of the total mass of NMHC sampled at the gas station. Thus, hexane seems to account for all branched C6 alkanes, while the large presence of butanes strongly minors the reactivity of the HC mixture from evaporations.

Industrial urban activities are strongly scattered in a city and cannot individually be compared with our measurements. We thus only discuss the total emissions associated to solvent use (SNAP 06) which have been extracted from our 5 km-wide urban area. The results are presented in Fig. 6c. They clearly underline the absence of ethylbenzene, 2-ethyltoluene, iso-propylbenzene in this sector of the inventory, which are known to be related to solvent activity (Dore et al., 2006; Rousseau, 2008) and which we have identified as strongly underestimated in the inventory compared to background urban measurements. This observation indicates that many reactive hydrocarbons are not accounted for in city centres, at least partly from urban diffuse sources, highlighting the need for an increased refinement of their representation.

3.3. Impact on ozone formation potential

We calculated the role of each hydrocarbon to the ozone formation potential of the air mass according to the equation given previously, for the average of the Atmo PACA measurements of June 2001 and for a weekday of the inventory. The results are presented in Fig. 7. In this figure, the OFPi of each hydrocarbon was normalized to the total OFP of the air mass. OFPi thus has no units, as it expresses a percentage of the total HC reactivity. The OFPi derived from the emission inventory, although calculated from emitted moles and not from molar ratios, are thus comparable with the OFPi derived from the observations. We notice in Fig. 7 that 3 types of hydrocarbons, that appear as the most susceptible to produce ozone in the city plume, are commonly pointed at by the inventory and by the measurements: toluene, xylenes and trimethylbenzenes. This constitutes a very positive point for the consistency of the global urban inventory speciation, in terms of urban photochemical reactivity. However, the disagreement on the m-p-xylene mass percentage appears to generate large differences in the air mass reactivity calculation. The same is observed for propene and iso-butene, despite their low relative abundances. Finally, the very uncommon 2-ethyltoluene appears to be a main element

of the reactivity speciation, which participates as largely as isopentane to the total OFP. The first 10 compounds in order of decreasing OFP, as revealed by this figure, constitute a critical ensemble of the emission inventory evaluation for urban areas. This list is essentially composed of aromatic hydrocarbons and alkenes.

When used in CTMs, such discrepancies may induce significant spatial and temporal variations in the quantity of ozone that is formed during the photochemical evolution of urban air masses. This point is examined in the next section.

4. Impact on CTM results

In this last section, we evaluated the sensitivity of the simulated regional ozone fields to inaccuracies in the urban emission inventory. In order to exclude large-scale influences in the observations, we selected periods with low wind, when the composition of the atmosphere of the city mainly resulted from surrounding emission forcing. The selected simulation period runs from June 20 to June 26, with a focus on the last 3 days that are associated with very low atmospheric dispersion conditions and regional ozone maxima that lie above the regulatory thresholds (Drobninski et al., 2007).

In order to observe the impact of the inventory inaccuracies on ozone production, we simulated the pollution episode several times, the first time with the original ESCOMPTE inventory, then with modified emission inventories. In these modified inventories, the HC urban speciation was modulated within the mean range of the disagreement factors calculated in the first part of this work. For each emission scenario, the total mass of HC emissions was maintained constant.

Besides the reference simulation conducted with the original emissions, a first type of scenarios (called HC17) was then generated, in which only the relative part of the 17 compounds presenting an important abnormality with regard to the measurements was modified. This modification was realized through the application, to the speciation profile, of 17 randomized coefficients lying in the 0.25–4 range which corresponds to the range where 90% of our disagreement factors lie. Such modifications were first applied to the road-traffic sector (scenario HC17_R) and then to all the sectors (HC17_A). These first scenarios aim to bring quantitative information on the effective sensitivity of ozone formation in CTMs due to the identified uncertainties in the emission speciation. A second set of emission scenarios (HC94_R and HC94_A) was then formed, in which the percentage

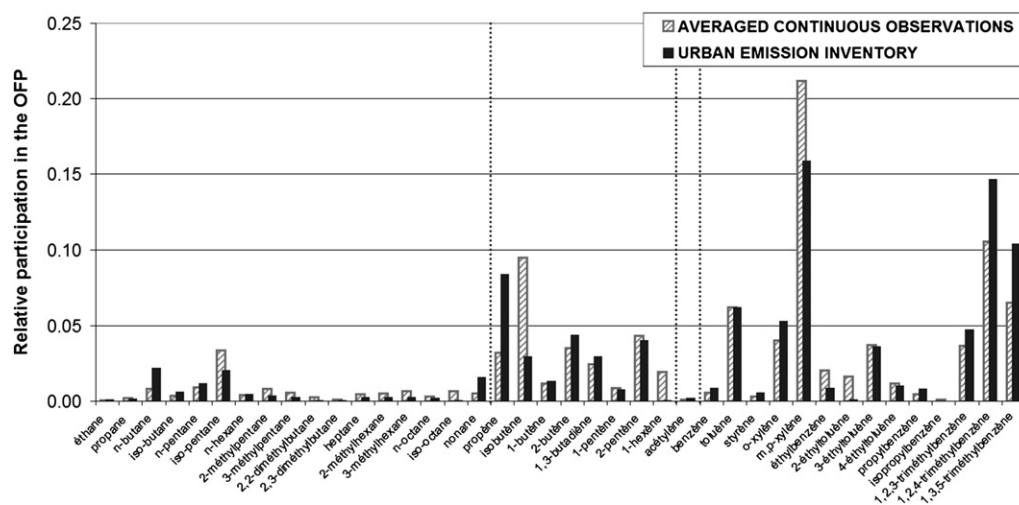


Fig. 7. Relative participation of each hydrocarbon to the total ozone formation potential, from observations (dashed grey) and from the inventory (black) for the 5 × 5 km urban area.

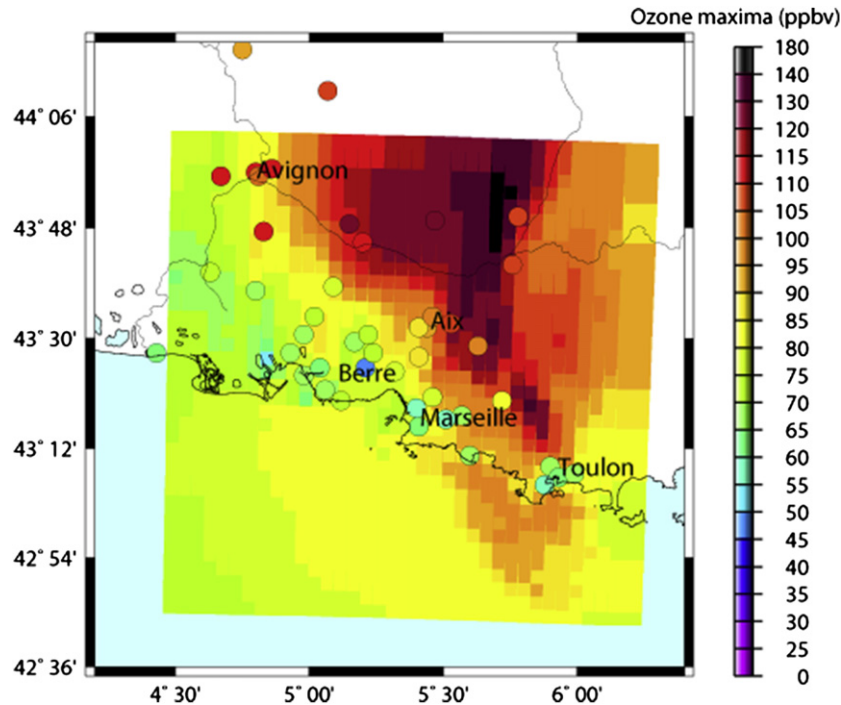


Fig. 8. Ozone maxima (in ppbv) simulated by CHIMERE for June 26, 2001 in each grid cell compared to ground-based observed maxima (coloured dots).

composition of all the 94 hydrocarbons of the inventory were perturbed. This second set of scenarios constitutes a less realistic set of situations, but it delimitates the theoretical sensitivity of the model to the HC emission speciations. Each of these 4 scenarios was conducted 4 times with a different randomized set of modulation factors, in order to observe the variability of the CTM answers to unpredictable disturbances.

Fig. 8 presents the ozone maxima simulated by CHIMERE on the ESCOMPTE area for June 26, compared with observations. During this day, the highest ozone values lie above the 120 ppbv regulatory ozone alert threshold. The oxidant plume forms downwind the urban coastal areas in the late morning, when pushed inland by the sea breeze that blows from the South. It is evacuated to the North of the domain, along the Durance valley, at the end of the afternoon.

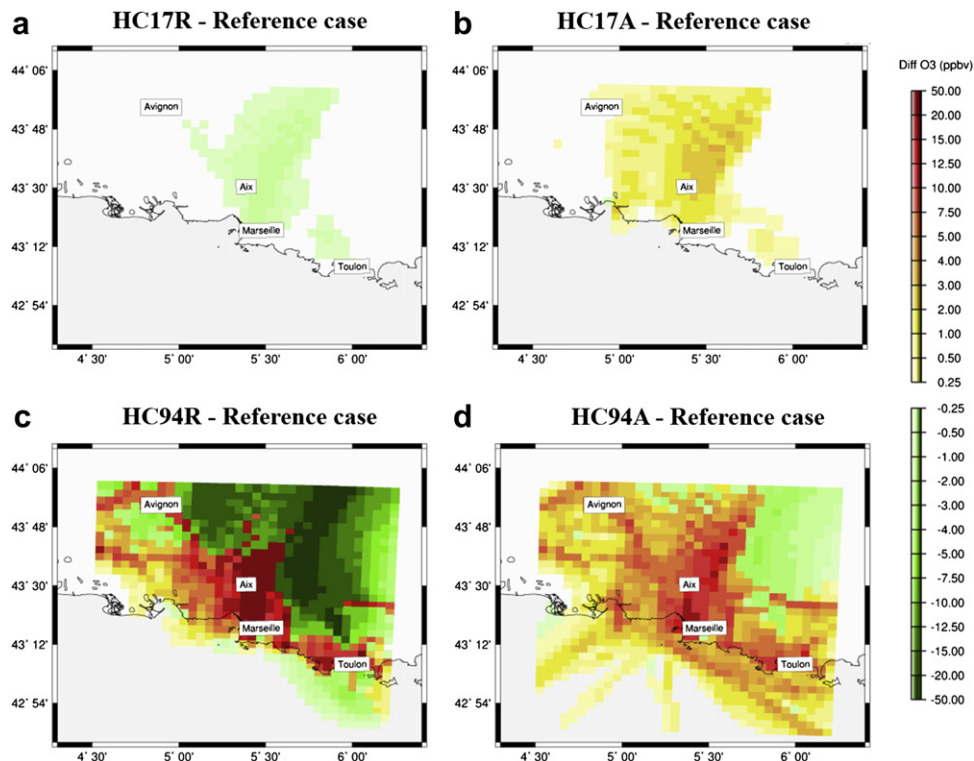


Fig. 9. Differences (in ppbv) in simulated ozone maxima with the reference case, for one example of each of the 4 emission scenarios (HC17R and A/HC94R and A).

Fig. 8 shows that the model quite well reproduces both the amplitude and the gradients in the diurnal ozone maxima all over the area, although the modelled plume is located too much at the East, probably due to a slight bias in the wind direction. Furthermore, no precise evaluation of the actual rural ozone maximum can be given by the few rural measurements sites. On the following figure (Fig. 9), we can see that the application of the randomized coefficients induces changes of highly variable amplitude in the model outputs, depending on the number of compounds and activity sectors that have been affected. The absolute impact on ozone dramatically increases from scenarios HC17 to HC94. In this last scenario, the differences (negative or positive) in simulated ozone maxima indeed reach several tens of ppbv with regard to the initial scenario, against less than 10 ppbv for the HC17 simulations. On the reverse, the average variations in ozone maxima are only slightly larger when coefficients are applied to all the activity sectors (A scenarios), than when only road traffic is affected (R scenarios). The variability inside a same scenario (conducted 4 times each with a different set of coefficients) is large however, but the figures shown here are representative of the absolute amplitude in ozone changes.

According to our previous analysis, HC17 simulations constitute the most realistic scenarios, while HC94 scenarios can be seen as indicators of the maximum effect of a wrong HC speciation on simulated ozone. Thus, although the overall sensitivity of simulated ozone to the emission speciation appears very large, our results indicate that the amplitude of the model response to realistic modulations of the emission speciation is moderate. It is however not insignificant. Indeed, a 10 ppbv value constitutes a prejudicial uncertainty in the domain of air-quality forecasting and analysis. Furthermore, the variability in the urban plume reactivity leads to geographical changes in the ozone plume, which can be formed closer to cities than in the reference case, and lead to biases in the ozone forecasts.

5. Conclusions

Our study consisted in the evaluation of the consistency of an urban state-of-the-art HC emission inventory. We focused on the 1 km-resolution inventory established within the framework of the ESCOMPTE program. The evaluation was processed through the comparison of this inventory with hourly HC measurements conducted during two summer months in the centre of Marseille on the Mediterranean French coast. This inventory takes into account the evolution of emissions during summer vacations. Hydrocarbon sampling experiments carried out close to urban emitters were also considered to analyze specific speciation profiles. In the light of the questions raised in the literature, we paid specific attention on the hydrocarbon speciation, which constitutes a critical element of the emission inventories. In a last step, we focused on the importance of HC emission speciation as inputs of chemistry-transport models for the forecast and the analysis of regional ozone concentrations.

Our results showed that, although the relative presence of the HC families in the urban atmosphere shows similarities with the emission inventory, strong disagreements are observed for several individual compounds. More precisely, most of the common and highly concentrated hydrocarbons (such as butanes) are too much predominant in the emission speciation. On the contrary, the heavy and less common species (branched alkanes, substituted aromatics) are under-represented in the inventory. We showed that the distribution of area sources (and in particular residential combustion) is a relevant issue at the local scale for hydrocarbons. This point supports the need of very local activity data, or empirical parameterizations not only depending on population density, for the distribution of emissions over a country. When considering individual sources, our results showed that the speciation of

road-traffic combustion emissions is rather well reproduced for the majority of the studied chemical families, although it suffers from the same bias. On the contrary, it appears that the urban diffuse sources, which are numerous, varied and little known, constitute a thorny point of the inventories, as was shown for the urban SNAP 06 emissions. Conversely to automobile combustion, these emissions are not very standardized and depend – even for their major components – on the exact nature of the activity. New advances on the distribution of such industrial activities in a city and on the definition of the associated HC speciation profiles appear necessary to refine the representation of the urban zones. However, the question of their validation remains opened, because of the difficulty to sample them either separately or globally.

The observed biases in the mean urban speciation profile have been shown to affect the reactivity of the inventory, and the subsequent regional ozone production. From an emission sensitivity study conducted with the eulerian CTM CHIMERE, we calculated an impact on ozone peaks of 6 ppbv at the maximum over the area, which remains moderate. Thus, without considering the total mass of HC emitted over the city, we can consider that current knowledge about HC emission speciation proposes a satisfactory representation of the urban hydrocarbon potential for ozone formation. However, supplementary work on HC emission profiles is still needed, as the case of the oxygenated VOCs (OVOCs) has not been considered, and that these very reactive compounds may be significantly present in urban emissions (residential combustion, commercial activities, transport, solvent use... as shown in Dore et al., 2006). Much work on urban OVOC inventories still remains to be done. Regional air-quality forecast would be the direct beneficiary of such improvements.

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